

STRUCTURED SURFACTANT SYSTEMS

The present invention relates to the formulation of structured surfactant suspending systems. It is particularly relevant to the formulation of laundry detergents especially those used for industrial and institutional cleaning.

STRUCTURED SURFACTANT

Suspending solids in liquids presents a problem. If the solids differ in density from the liquid they will tend either to sediment or float. Increasing the viscosity of the liquid can retard, but not prevent such separation, and high viscosities are generally undesirable. Colloidal systems, in which the suspended particles are sufficiently small to experience Brownian motion, e.g. less than 1 micron, may be kinetically stable. However the difficulty or undesirability of comminuting some solids to such sizes, and the impossibility of maintaining many of them at this level in the face of crystal growth or agglomeration, limits the use of colloidal suspensions.

Adjusting the density of one phase to match that of the other is usually impracticable. Moreover such systems are almost always temperature-unstable due to differential rates of thermal expansion.

One method of suspension which permits even relatively large particles to be stably suspended is structured surfactant. The term covers systems in which a surfactant mesophase, usually a lamellar or G-phase, alone or more usually interspersed with an aqueous phase, provides a yield stress which is sufficient, when the system is at rest, to immobilise any suspended particles, but which is sufficiently low to allow the system to be poured like a normal liquid. Such systems may display very low apparent viscosities when stirred, pumped or poured and yet be capable of maintaining particles, sometimes of millimetre or larger size, indefinitely in suspension.

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Three main types of suspending system have been employed in practice, all involving a G-phase, in which bilayers of surfactant are arranged with the hydrophobic part of the molecule on the interior and the hydrophilic part on the exterior of the bilayer (or vice versa). The bilayers lie side by side, e.g. in a parallel or concentric configuration, sometimes separated by aqueous layers. G-phases (also known as L_{α} phases) can usually be identified by their characteristic textures under the polarising microscope and/or by x-ray diffraction, which is often able to detect evidence of lamellar symmetry. Such evidence may comprise first, second and sometimes third order peaks with d-spacing ($\frac{2\pi}{Q}$ where Q is the momentum transfer vector) in a simple integral ratio 1:2:3. Other types of symmetry give different ratios, usually non integral.

Most surfactants form a G-phase either at ambient or at some higher temperature when mixed with water in certain specific proportions. However such G-phases cannot usually be used as structured suspending systems. Useful quantities of solid render them unpourable and smaller amounts tend to sediment.

The main types of structured system used in practice are based on dispersed lamellar, spherulitic and expanded lamellar phases. Dispersed lamellar phases are two phase systems in which the surfactant bilayers are arranged as parallel plates to form domains of G-phases which are interspersed with an aqueous phase to form an opaque gel-like system. They are described in EP O 086 614.

Spherulitic phases comprise well defined spheroidal bodies, usually referred to in the art as spherulites, in which surfactant bilayers are arranged as concentric shells. The spherulites usually have a diameter in the range 0.1 to 15 microns and are dispersed in an aqueous phase in the manner of a classical emulsion, but interacting to form a structured system. Spherulitic systems are described in more detail in EP O 151 884.

Many structured surfactant systems are intermediate between dispersed lamellar and spherulitic, involving both types of structure. Usually systems having a more spherulitic character are preferred because they tend to have lower viscosity. A variant on the spherulitic system comprises prolate or rod shaped bodies sometimes referred to as batonets.

A third type of structured surfactant system comprises an expanded G-phase. It differs from the other two types of structure system in being essentially a single phase, and from conventional G-phase in having a wider d-spacing. Conventional G-phases have a d-spacing of about 5 to 7 nanometers. Attempts to suspend solids in such phases results in stiff pastes which are either non-pourable, unstable or both. Expanded G-phases with d-spacing between 8 and 20, e.g. 10 to 15 nanometers, form when the electrolyte is added to aqueous surfactants at concentrations just below those required to form a normal G-phase, particularly to surfactants in the M phase. The M phase comprises surfactant molecules arranged to form cylindrical rods of indefinite length. It exhibits hexagonal symmetry and a distinctive texture under the polarising microscope. Typical M phases have so high a viscosity that they appear to be curdy solids. M phases near the lower concentration limit (the L_1 /M phase boundary) may be pourable but have a very high viscosity and often a mucous-like appearance. Such systems tend to form expanded G-phases particularly readily on addition of sufficient electrolyte.

Expanded G-phases are described in more detail in EP O 530 708. In the absence of suspended matter they are translucent, unlike dispersed lamellar or spherulitic phases which are necessarily opaque. They are optically anisotropic and have shear dependent viscosity. In this they differ from L_1 phases which are micellar solutions and which include microemulsions. L_1 phases are clear, optically isotropic and substantially Newtonian. They are unstructured and cannot suspend solids. Some L_1 phases exhibit small angle x-ray diffraction spectra which show evidence of hexagonal symmetry. Such phases usually have concentrations near the L_1 /M phase boundary and may form expanded G-phases on addition of electrolyte.

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Most structured surfactant systems require the presence of electrolyte as well as surfactant and water in order to form structured systems capable of suspending solids. However certain relatively hydrophobic surfactants such as isopropylamine alkyl benzene sulphonate can form spherulites in water in the absence of electrolyte. Such surfactants are capable of suspending solids in the absence of electrolyte as described in EP O 414 549.

APPLICATION

Structured surfactants have been applied to the problems of suspending: water insoluble or sparingly soluble builders in laundry detergent; antifoams and enzymes in laundry detergents and other surfactant systems; abrasives in hard surface cleaners; pesticides and oils in agrochemical preparations (EP O 388 239 and EP O 498 231); rock cuttings in drilling muds (EP O 430 602); dyestuffs in dye bath concentrates and printing inks (EP O 472 089); talcs, oils and other cosmetic ingredients in personal care formulations (EP O 530 708).

FLOCCULATION

A problem with the two phase structured surfactant systems, and especially spherulitic systems, is flocculation of the dispersed surfactant structures. This tends to occur at high surfactant and/or high electrolyte concentration. It can have the effect of making the composition very viscous and/or unstable with the dispersed surfactant separating from the aqueous phase.

Certain amphiphilic polymers have been found to act as deflocculants of structured surfactants. One type of deflocculant polymer exhibits cteniform (comb-shaped) architecture with a hydrophilic backbone and hydrophobic side chains or vice versa. A typical example is a random copolymer of acrylic acid and a fatty alkyl acrylate. Cteniform deflocculants have been described in a large number of patents, for example WO-A-9106622.

A more effective type of deflocculant has surfactant rather than cteniform architecture. With a hydrophilic polymer group attached at one end to a hydrophobic group. Such deflocculants are typically telomers formed by telomerising a hydrophilic monomer with a telogen having a hydrophobic group. Examples of surfactant deflocculants include alkyl thiol polyacrylates and alkyl polyglycosides. Surfactant deflocculants are described in more details in EP O 623 670.

THE PROBLEM

A disadvantage of both surfactant and cteniform deflocculants is that the concentration required to deflocculate to optimum viscosity is critical within fairly narrow limits and varies with temperature. Either too little or too much deflocculant causes instability and/or excessive viscosity. As a result the deflocculated systems tend to separate if the temperature varies significantly.

One approach to the problem of temperature stability has been to add highly cross linked polyacrylates (see US 5 602 092). These are difficult to disperse in the structured liquid.

Another problem is the high cost of the deflocculants and their tendency to promote foaming, which often requires the addition of antifoams.

A particular problem arises in relation to liquid detergents suitable for use in industrial and institutional laundries, such as factories, hospitals and hotels and especially in automatically dosed washing machines.

An ideal laundry detergent for institutional use would combine: high surfactant levels and in particular high levels of non-ionic surfactant, which has been found particularly effective for removing soil; high alkalinity, to saponify fatty soil; and high levels of builder, which improve the performance of the surfactant by counteracting the effects of calcium in the water. The composition must be

homogeneous and pourable and the concentration as high as possible. Unfortunately it is generally difficult to combine surfactants with electrolytes at high concentrations to form stable compositions. It has proved particularly difficult to achieve this with non-ionic surfactants which are not capable of forming stable solutions at high alkalinity or in the presence of electrolyte, except at very low concentrations which are too low to be commercially acceptable. As a consequence it has hitherto been customary to use two separate solutions in institutional machines, one to supply the surfactant and a separate solution as the source of the alkali.

Attempts to combine the two in a single formulation have hitherto been unsuccessful. Even the use of a deflocculant such as those described in EP-A-0 623 670 or EP-A-0 346 995 has not been successful in forming a sufficiently stable homogeneous phase of commercially acceptable concentration, or has done so only over a very restricted temperature range.

THE SOLUTION

We have now discovered that water soluble carbohydrates are capable of deflocculating dispersed lamellar or spherulitic structured surfactant systems. They are substantially cheaper than known deflocculants and do not cause excessive foaming. They are generally less sensitive to temperature variations.

THE INVENTION

Our invention provides a structured surfactant composition capable of suspending solids which comprises surfactant, water and, if required, electrolyte in relative proportions adapted to form a flocculated, dispersed lamellar and/or spherulitic structured surfactant system, and, in addition, sufficient of a deflocculant to inhibit the flocculation of said system characterised in that said deflocculant comprises a water-soluble carbohydrate.

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Preferably said surfactant consists of a major amount of non-ionic surfactant and optionally a minor amount of anionic and/or amphoteric. Said water is preferably present in a proportion of from 20 to 60%, especially 30 to 50%. Said electrolyte preferably comprises alkali. Said deflocculant preferably comprises at least 10% by weight of the composition of a mono- or preferably di-saccharide.

THE AUXILIARY STABILISER

The composition may contain an auxiliary stabiliser to prevent or inhibit temperature instability such as bottom separation or phase changes on warming. The stabiliser may comprise (i) an ethoxylated C₈₋₂₀, straight or branched chain alcohol or fatty acid, fatty amine, sorbitan or glycerol ester, alkyl polypropoxy group or alkyl phenyl group and (ii) a water soluble thiocyanate. The number of ethoxy groups may be from 20 to 100, e.g. 30 to 80, preferably 40 to 60. The mole ratio of (i):(ii) may preferably be from 1:100 to 10:1, e.g. 1:50 to 5:1.

The total concentration of auxiliary stabiliser may typically be from 5 to 150% molar based on the deflocculant, e.g. 10 to 100%. The concentration of (B) in the composition is preferably from 0.1 to 10%, e.g. 0.5 to 5%, especially 0.8% to 2%.

THE CARBOHYDRATE

The term "carbohydrate" as used herein includes mono-, di-, and oligosaccharides, water soluble polysaccharides and also water soluble non-surfactant derivatives of the saccharides such as carboxylic acids, e.g. gluconic, mannitol and ascorbic acids and alginates, reduced sugars such as sorbitol, mannitol or inositol and dialdehyde starches.

Preferred deflocculants are sorbitol, alginates, soluble starches and mono and di-saccharides. The alginates are preferably alkali metal or ammonium salts e.g. sodium alginate. They are preferably present in concentrations of from 0.05 to 5%, e.g. 0.1 to 2% especially 0.2 to 1%.

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The mono and di-saccharides and derivatives such as sorbitol are usually required in much higher proportions than polysaccharide deflocculants. Generally concentrations of more than 5% by weight of the composition are required, more usually 10 to 20%, especially 12 to 18%.

The di-saccharide is preferably sucrose but may also be, for example, maltose, lactose or cellobiose. Other carbohydrates for use in the invention include glucose, fructose, mannose, ribose, galactose, alldose, talose, gulose, idose, arabinose, xylose, lyxose, erythrose, threose, acrose and rhamiose.

INSTITUTIONAL AND INDUSTRIAL FORMULATIONS

According to a preferred embodiment the invention provides a detergent composition comprising:-

- (A) 20 to 75% by weight of the composition of water;
- (B) At least 3% based on the weight of the composition, preferably 4 to 10%, surfactant comprising more than 50% based on the total weight of surfactant of non-ionic surfactants having a mean HLB of from 10 to 15 and optionally a smaller proportion of anionic and/or amphoteric surfactant;
- (C) At least 10% by weight based on the weight of the composition of builders;
- (D) At least 7% based on the weight of the composition of dissolved non-micelle-forming salts and bases which dissociate at least partially in solution into ions, including any dissolved portion of said builder;
- (E) A total free alkalinity of at least 0.5 normal;

- Wherein said deflocculant comprises a water soluble carbohydrate.

The surfactant is preferably all non-ionic since in some applications inclusion of anionic surfactant can adversely affect performance. However where anionic surfactant can be tolerated its inclusion has the advantage of enabling higher total concentrations of surfactant to be more easily achieved. Typically wholly non-ionic based formulations contain from 7 to 30%, more typically 10 to 25% by weight surfactant while compositions containing a minor proportion of anionic surfactant may contain up to 50% by weight, e.g. 15 to 40%, especially 20 to 35%.

The non-ionic surfactant preferably consists of from 60 to 100% by weight of alkoxyate, preferably ethoxyate or mixed ethoxyate/propoxyate. Typically it comprises alkoxyated C₈₋₂₀, especially C₁₀₋₁₈ natural or synthetic alcohols. The alcohols are typically primary or secondary, straight or branched chain, saturated or unsaturated. Also effective are alkoxyated fatty acids, fatty amines, alkyl phenols, glyceryl mono and dialkyl esters and sorbitan esters.

The ethoxylate typically contains an average of from 1 to 10 alkoxy groups depending on the alkyl chain length, to give an HLB of from 10 to 15, preferably 12 to 14.

The non-ionic surfactant may comprise a mono- or di- ethanolamide or an amine oxide. The surfactant may optionally contain a minor proportion (i.e. less than 50% based on the total weight of surfactant) of anionic surfactant such as soap and/or

The builder is preferably sodium tripolyphosphate, but may alternatively be or comprise sodium or potassium pyrophosphate, sodium or potassium citrate, sodium or potassium carbonate or a zeolite. Other builders include EDTA, nitrilotriacetate, phosphonates and poly electrolytes such as polyacrylates or polymaleates. The term "builder", as used herein, excludes any hydroxides used to provide the free alkali but includes carbonate and silicate. The builder is present in amounts greater than 10% by weight based on the total weight of the composition, preferably more than 15%. Levels of builder may be above 20%, any excess over the solubility in the system being present as suspended particles. Builder concentrations do not normally exceed 50% by weight and are usually less than 40%, e.g. less than 30%.

The composition contains a total of at least 7% by weight of dissolved surfactant desolubilising salts and bases. This includes any dissolved portion of the builder and any alkali required to provide the free alkalinity.

It excludes micelle forming components such as an anionic surfactant. The dissolved salts and bases preferably constitute from 10 to 40%, e.g. 15 to 30% by weight of the composition, and sufficient to form a multiphase system in which an aqueous phase is interspersible with a surfactant or surfactant mesophase.

The total free alkali should be sufficient to neutralise at least an equal volume of 0.5 normal HCl. Preferably the free alkalinity is from 0.7 to 2 normal, e.g. 0.8 to 1.5.

The alkyl polyglycoside is preferably a polyglucoside and typically has an average degree of polymerisation between 1.3 and 10, more usually 1.5 to 3. The alkyl polyglycoside is generally added in an amount sufficient to provide an interspersion of the aqueous phase with the surfactant phase at 25°C. which does not separate within 1 month. This may typically require from 0.5 to 10, more usually 1 to 5%, e.g.

2 to 4.5% by weight based on the weight of the composition. The amount is preferably adjusted to obtain a spherulitic composition comprising surfactant vesicles, usually having a multilamellar or G-phase structure, dispersed in an aqueous phase.

We particularly prefer that compositions of the invention contain an auxiliary stabiliser which helps to extend the range of temperature within which the composition is stable. This may be particularly desirable where storage at relatively high temperatures, e.g. 40°C, is an important consideration. The auxiliary stabiliser may be an ethoxylated alcohol having an average of 20 to 100, more usually 25 to 75, e.g. 30 to 60 ethylene oxide groups per molecule, together with a thiocyanate especially potassium thiocyanate. Alternatively the auxiliary stabiliser may be a polycarboxylate having on or more alkyl groups such as C₈₋₂₀ alkyl thiol polycarboxylate e.g. polyacrylate or polymaleate, or a copolymer of unsaturated carboxylic acid with a C₈₋₂₀ alkyl ester of unsaturated carboxylic acid e.g. a copolymer of acrylic acid and/or maleic acid with a minor proportion of a C₈₋₂₀ alkyl acrylate and/or alkyl maleate ester.

The auxiliary stabiliser may be present in proportions up to 5% by weight, usually 0.01 to 3%, e.g. 0.02 to 2 especially 0.01 to 1. Combinations of two or more auxiliary stabilisers may sometimes be particularly effective.

The detergent compositions of the invention preferably also contain the conventional minor detergent ingredients including antifoams such as silicone antifoam, soil suspending agents such as a carboxymethyl cellulose, optical brighteners, stain removers such as enzymes, bleaches including perborate metaborate mixtures, sequestrants such as phosphonates and especially amino phosphonates including aminotrismethylene phosphonate, ethylene diamine tetrakis (methylene phosphonate), diethylene triamine pentakis (methylene phosphonate) and others in the same series, perfumes, colouring, preservatives, corrosion inhibitors, bleach activators such as TAED and/or fabric conditioner.

The aforesaid minor ingredients may all be present in conventional amounts and usually constitute a total of less than 5% by weight of the composition, typically less than 1%. The anionic component of the ionic ingredients may typically be sodium, potassium or a mixture of the two. Potassium is preferred where very high solids contents are desired.

The invention is illustrated by the following examples in which all proportions are by weight of the 100% material based on the weight of the composition.

EXAMPLE 1

	% wt/wt
Optical brightener "TINOPAL" ® CBS/X	0.05
C ₁₂₋₁₄ alkyl two mole ethoxylate	3.75
C ₁₂₋₁₄ alkyl seven mole ethoxylate	3.75
Potassium thiocyanate	0.5
C ₁₂₋₁₈ fifty mole ethoxylate	0.5
Sodium alginate	0.5
Sodium tripolyphosphate	22.5
Formaldehyde	0.05
Water	balance

The above laundry detergent formulation was stable over extended storage periods at ambient, elevated (40°), low (2°) and cycled temperatures and readily pourable. The washing performance was similar to those obtained using either C₁₂₋₁₄ alkyl thiol polyacrylate or alkyl polyglycoside as the deflocculant however use of either of the two latter resulted in excessive foaming, necessitating the addition of an antifoam. The thiol polyacrylate required slightly higher concentrations, and the polyglycoside much higher concentrations, to achieve equivalent viscosity and stability.

When the thiocyanate and/or the fifty mole ethoxylate were omitted from the formulation or from either of the comparative formulations, the resulting products were unstable when stored under fluctuating or elevated temperature conditions.

EXAMPLE 2

	% wt/wt
Optical brightener "TINOPAL" ® CBS/X	0.05
C ₁₂₋₁₄ alkyl two mole ethoxylate	3.75
C ₁₂₋₁₄ alkyl seven mole ethoxylate	3.75
Potassium thiocyanate	0.5
C ₁₂₋₁₈ alkyl fifty mole ethoxylate	0.5
Sucrose	15.0
Sodium tripolyphosphate	22.5
Formaldehyde	0.05
Water	balance

The above laundry detergent formulation was stable when stored at ambient, elevated (40°), depressed (2°) and cycled temperatures, was readily pourable and gave washing performance comparable to that of Example 1. Excessive foaming was not observed.

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EXAMPLE 3 AND 4

The following laundry detergent compositions are stable, pourable, non -flocculated suspensions.

	<u>Ex 3</u>	<u>Ex 4</u>
C ₁₂₋₁₄ alkyl 6 mole ethoxylate	11.5	11.5
C ₁₂₋₁₅ branched alkyl 3 mole ethoxylate	1.0	1.0
C ₁₂₋₁₄ alkyl polyglucoside (d.p. 1.6)	2.8	2.7
sodium tripolyphosphate	22.0	22.0
sodium hydroxide	7.0	7.0
sodium silicate	1.0	1.0
sorbitol	15.0	2.0
optical brightner "TINOPAL"® cbs/x	0.1	0.1
polyvinyl pyrrolidone	-	0.05
silicone antifoam	0.1	0.1
sodium triethylenetetramine		
pentapethylen phosphonate	0.25	-
Conductivity	15.2mS	31.6mS
Viscosity	4000cp	2000cp
Sisko Index	0.59	0.4